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Review

Progress on rare-earth doped ZnO-based varistor materials

Feng JIANG[a], Zhijian PENG[a,*], Yanxu ZANG[a], Xiuli FU[b,*]

[a]*School of Engineering and Technology*, *China University of Geosciences*, *Beijing 100083*, *P.R. China*
[b]*School of Science*, *Beijing University of Posts and Telecommunications*, *Beijing 100876*, *P.R. China*

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Abstract: Rare-earth (RE) doping can greatly enhance the voltage gradient of ZnO-based varistors, and their nonlinear coefficient, leakage current, energy absorption capability, through-current capability and residual voltage can also be improved to certain extent. In this review, the progress on RE-doped ZnO-based varistor materials in recent years was summarized. The mechanism of RE doping on the electrical performance of ZnO varistors was analyzed. The issues in exploring new ZnO-based varistor materials by RE doping were indicated, and the development trends in this area were proposed.

Keywords: ZnO varistor; rare-earth (RE); doping

1 Introduction

Zinc oxide (ZnO) varistors are well-known electronic devices, which are ceramic semiconductors by sintering ZnO with a small amount of additives. The famous properties of ZnO varistors are their highly nonlinear *I–V* characteristics (non-ohmic behavior) and excellent surge tolerance. ZnO varistors have large nonlinear coefficient, short responding time, low leakage current and so on. In normal use, they are subject to a voltage below their characteristic voltage and pass only a leakage current. When the voltage exceeds the switch voltage, for instance, during a voltage transient or surge, the varistor becomes highly conducting and draws the current through it, usually to ground. When the voltage returns to normal, the varistor returns to its highly resistive state. And this procedure is reversible with little or even no hysteresis. Because of the excellent electrical characteristics, surge arresters using ZnO nonlinear elements have been replacing those using silicon carbide nonlinear elements, and are being rapidly promoted for various applications. Now they can be used in AC or DC fields over a wide range of voltage, from a few volts to tens of kilovolts, and a wide range of current, from microamperes to kiloamperes, both in power industry and in semiconductor industry, establishing a reliable service record and good reputation [1,2].

Due to the special working environment (high current shock) of ZnO varistors, coupled with the demand of metal oxide surge arresters of large capacity and miniaturization (small size) under ultra-high voltage, it is desirable to develop ZnO varistors of a good comprehensive electrical property with low residual voltage, good nonlinear performance, high through-current capability, high energy absorption capacity, low leakage current and higher voltage gradient [3,4].

In recent years, a large number of researches have been carried out by scientists to improve the

* Corresponding authors.
E-mail: Zhijian Peng, pengzhijian@cugb.edu.cn;
Xiuli Fu, xiulifu@bupt.edu.cn

performance of ZnO varistors, and the ways for them can be summarized as follows [2–7]: (1) adjustment and optimization of material prescriptions in order to design and tailor the material composition and microstructure; (2) improvement of powder technology to enhance the powder homogeneity in composition and structure, and powder formability, thus ultimately increasing the homogeneity in composition and structure of the prepared varistors; (3) optimization and improvement of sintering methods and processing parameters to lower the sintering temperature, reduce the porosity of sintered bodies, achieve varistor materials with more homogeneous and smaller grains, and lessen the volatilization of effective components in the materials; and (4) other improvements in, such as the forming methods and processing parameters of varistor green bodies, the preparation methods and processing parameters of the varistor electrodes, the design and optimization of new architecture of varistors, and so forth. Among them, the method of rare-earth (RE) doping developed since the 1970s creates a unique opportunity for improving the nonlinear performance of ZnO varistors.

RE-doped ZnO varistor materials have the following advantages [8–12]. (1) Compared with the doping by other elements (under the same conditions), RE doping into ZnO varistors can significantly increase the voltage gradient of varistors. Thus it is possible to reduce the volume of varistors under the same application conditions. And it can also simplify the tank structure of gas insulated switchgear from metal oxide arrestors (GIS-MOA), enhance the location flexibility of resistors, optimize the structure and configuration of GIS, and acquire varistor devices with less weight and smaller size [8]. (2) RE doping can increase the nonlinear coefficient and decrease the leakage current of varistors, especially when ZnO–Pr_6O_{11}-based varistors are prepared [9]. Compared to the undoped one, RE doping can often greatly increase the nonlinear coefficient of ZnO–Pr_6O_{11}-based varistors and reduce their leakage current to certain extent, thus improving the ability of the thermal shock resistance and extending the service life of varistors. (3) The doped RE oxides can act as grain growth inhibitors to ZnO grains during sintering, thus improving the voltage gradient of varistors without reducing their energy absorption capacity; meanwhile, they can also increase the through-current capability and reduce the residual voltage of varistors, finally improving the resistor qualities [8,10–12]. In this review, the progress on RE-doped ZnO-based varistor materials in recent years is summarized.

2 RE doping effect on voltage gradient of ZnO varistors

The voltage gradient of ZnO varistors (also called varistor voltage in the literature) can be significantly improved by RE doping. Shichimiya *et al*. [8] studied the doping effect of different RE elements on the voltage gradient of ZnO–Bi_2O_3 varistors with the same amount (seen in Fig. 1). Typically, the voltage gradient of undoped ZnO–Bi_2O_3 varistors is approximately 150–200 V/mm. However, after doped with certain amount of REs, the voltage gradient of the varistors can be increased up to 1–1.5 times under the doping and processing conditions as reported in Ref. [8].

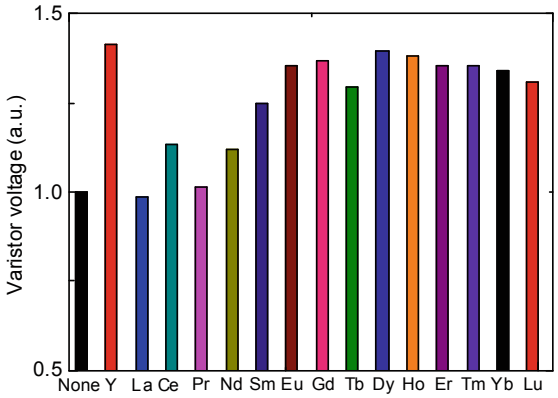

Fig. 1 Effect of RE doping on the voltage gradient of ZnO–Bi_2O_3 varistors [8].

Many scientists have performed extensive researches on the doping effects of different types of REs into ZnO varistors. By optimizing the doping amount of REs and corresponding sintering processes, ZnO varistors with high voltage gradient have been developed. Typical results are listed in Table 1.

A large number of facts have shown that the voltage gradient of ZnO varistors could be significantly increased after the increasing amount of REs is doped, but too much of REs would result in decreased voltage gradient of ZnO varistors [24–28]. So, normally, an optimum doping amount of REs should be reached during developing such kind of ZnO varistors.

The cause of voltage gradient increase of ZnO varistors by RE doping is also investigated by many scientists [29–34]. Generally, it is believed that the ionic radius of REs is greater than that of Zn^{2+} ions.

Table 1 Voltage gradients of ZnO-based varistors doped with optimum amount of different REs

Practical composition			Sintering system	E_{max} (V/mm)	Ref.
Basic component[a]	RE doped	Other additives			
81.84 wt%ZnO+ 2.79 wt%Bi_2O_3	7 wt%Pr_6O_{11}	5.58 wt%Sb_2O_3+0.465 wt%Cr_2O_3+ 1.395 wt%Co_2O_3+0.93 wt%MnO_2	1150–1200 ℃, 2 h	444[c]	[13–15]
96.9 mol%ZnO+ 0.7 mol%Bi_2O_3	0.1 mol%Y_2O_3	1.0 mol%Sb_2O_3+0.8 mol%Co_2O_3+ 0.5 mol%(MnO_2+Cr_2O_3)	800 ℃, 2 h	2197[b]	[16,17]
96.5 mol%ZnO+ 0.5 mol%Pr_6O_{11}	2.0 mol%Nd_2O_3	1.0 mol%CoO	1300 ℃, 1 h	584.1[b]	[18]
96.4 mol%ZnO+ 0.7 mol%Bi_2O_3	0.1 mol%Dy_2O_3	1.0 mol%Sb_2O_3+0.8 mol%Co_2O_3+ 0.5 mol%(MnO_2+Cr_2O_3)	800 ℃, 2 h	3019[b]	[19]
96.5 mol%ZnO+ 0.7 mol%Bi_2O_3	0.5 mol%Er_2O_3	1.0 mol%Sb_2O_3+0.8 mol%Co_2O_3+ 0.5 mol%(MnO_2+Cr_2O_3+NiO)	800 ℃, 2 h	2025[b]	[20]
97 mol%ZnO+ 0.5 mol%Pr_6O_{11}	1.0 mol%Tb_4O_7	1.0 mol%CoO+0.5 mol%Cr_2O_3	1300 ℃, 1 h	845.1[b]	[21]
97 mol%ZnO+ 0.5 mol%Pr_6O_{11}	1.0 mol%La_2O_3	1.0 mol%CoO+0.5 mol%Cr_2O_3	1230 ℃, 1 h	777.9[b]	[22]
95.25 mol%ZnO+ 1.0 mol%Bi_2O_3	1.2 mol%Ho_2O_3	0.5 mol%Co_2O_3+0.5 mol%$MnCO_3$+ 0.5 mol%Cr_2O_3+1.0 mol%Sb_2O_3+ 0.05 wt%$Al(NO_3)_3{\cdot}9H_2O$	1180 ℃, 2 h	504[c]	[23]
96.44 mol%ZnO+ 0.7 mol%Bi_2O_3	0.06 mol%CeO_2	1.0 mol%Sb_2O_3+0.8 mol%Co_2O_3+ 0.5 mol%MnO_2+0.5 mol%Cr_2O_3	1100–1200 ℃	~460[b]	[24]

(*a*) Including ZnO, and Bi_2O_3 or Pr_6O_{11} which induce nonlinear properties; (*b*) the properties were measured at a current density of 1.0 mA/cm^2; (*c*) the data were measured at a current density of 0.25 mA/cm^2.

During sintering, RE oxides tend to segregate ZnO grain boundary, pinning ZnO grains, thus inhibiting the growth of ZnO grains [29–33]. There is also a viewpoint that after RE doping, a new spinel phase (possibly, containing REs) with small grains is formed, evenly distributing over the materials, and due to the pinning effect of the newly formed spinel phase, the growth of matrix ZnO grains is inhibited, thus raising the voltage gradient of ZnO varistors [31–34]. However, too much of REs would result in excessive accumulation of inter-granular phase, reducing the densification of the materials and their structure homogeneity, thus leading to decreased voltage gradient of ZnO varistors [28,29].

Bernik *et al*. [35] also found that, in order to improve the voltage gradient of ZnO varistors, some REs have to cooperate with other additives. For example, in ZnO–Bi_2O_3-based varistors, if there is no synergistic effect of Sb_2O_3, the doped Y_2O_3 will form solid solution phase of Bi–Y–O ($Bi_{1.9}Y_{0.1}O_3$) with Bi_2O_3, which cannot effectively restrain the growth of ZnO grains, thus resulting in ZnO varistors with a relatively low voltage gradient. This work confirmed that, the average size of ZnO grains without Sb_2O_3 doping in such material system is two times greater than that under co-doping with Y_2O_3 and Sb_2O_3. So, the voltage gradient of the former varistor is much lower.

There are still problems existing in how to increase the voltage gradient of ZnO varistors by RE doping. (1) As RE doping may lead to nonuniform distribution of oxygen, a “soft heart” phenomenon (i.e., the electrical properties of varistors are inconsistent between the inside and outside of the materials) [36–38] will happen obviously in large-size ZnO–Bi_2O_3 ceramic varistors. So the optimization of preparation processes, in particular, spray granulation process and sintering process, to improve the uniformity of the inside and outside structures of the materials, is one of the focuses in this field in the future. (2) Due to the

complicated mechanism of RE doping on ZnO varistors and the versatility of REs, to develop new-formula high-performance ZnO varistors with optimum doping amount of REs, avoiding misuse and abuse of RE doping which may lead to decreased voltage gradient of ZnO varistors, and to ascertain the mechanism of RE doping are another research focuses of this area in the future.

3 RE doping effect on nonlinear coefficient of ZnO varistors

The nonlinear coefficient of ZnO varistors will directly determine the capability of the varistors to restrict instantaneously high voltage surge, thus it is very important to improve the nonlinear coefficient of varistors. In recent years, many authors have reported their investigations on RE doping into ZnO varistors. Table 2 lists some of the important results on improving the nonlinear coefficient of typical ZnO varistors in the literature.

It is generally believed that the grain boundary effect is the root cause of nonlinear characteristics of ZnO varistors. The grain boundary properties, such as donor concentration, interface state density and barrier height, have significant effects on the nonlinear electrical property of ZnO ceramic varistors. For example, the higher the barrier height of a varistor, the larger the nonlinear coefficient [51–53]. Typically, the ionic radius of RE elements is greater than that of Zn^{2+} ions. So during sintering, the doped RE oxides or their reaction products will normally segregate ZnO grain boundaries. However, during RE doping, the substitution of Zn^{2+} ions in ZnO grains by certain amount of the doped RE atoms will still happen, thus resulting in defects in ZnO grains, and during the substituting reaction, oxygen may be produced, thus affecting the donor concentration. Usually, the higher the partial pressure of oxygen, the lower the donor concentration. As the donor concentration decreases, the interface state density of the varistors will also be diminished, eventually leading to enhanced barrier height, thus increasing the nonlinear coefficient of ZnO varistors [16,53,54]. Moreover, the substituting reaction may also produce electrons, which will be of

Table 2 Nonlinear coefficients of ZnO varistors doped with optimum amount of different REs

Practical composition			Sintering system	α_{max}	Ref.
Basic composition	RE doped	Other additives			
81.84 wt%ZnO+ 2.79 wt%Bi_2O_3	7 wt%Pr_6O_{11}	5.58 wt%Sb_2O_3+0.465 wt%Cr_2O_3+ 1.395 wt%Co_2O_3+0.93 wt%MnO_2	1150–1200 ℃, 2 h	77[c]	[13–15]
97.5 mol%ZnO+ 0.5 mol%Pr_6O_{11}	1.0 mol%Nd_2O_3	1.0 mol%CoO	1300 ℃, 1 h	65.2[a]	[18]
97 mol%ZnO+ 0.5 mol%Pr_6O_{11}	1.0 mol%Tb_4O_7	1.0 mol%CoO+0.5 mol%Cr_2O_3	1300 ℃, 1 h	52[a]	[21]
95.65 mol%ZnO+ 1.0 mol%Bi_2O_3	0.8 mol%Ho_2O_3	0.5 mol%Co_2O_3+0.5 mol%$MnCO_3$+ 0.5 mol%Cr_2O_3+1.0 mol%Sb_2O_3+ 0.05 wt%$Al(NO_3)_3{\cdot}9H_2O$	1180 ℃, 2 h	82[b]	[23]
94.316 mol%ZnO+ 0.5 mol%Bi_2O_3	0.9 mol%CeO_2	1.2 mol%Sb_2O_3+0.5 mol%Co_2O_3+ 1.0 mol%MnO_2+0.5 mol%Cr_2O_3+ 0.5 mol%Ni_2O_3+0.5 mol%SiO_2+ 0.08 mol%B_2O_3+0.004 mol%Al_2O_3	1175 ℃, 2 h	~30[b]	[30]
90.0 mol%ZnO+ 0.5 mol%Pr_6O_{11}	4.0 mol%Y_2O_3	5.0 mol%CoO+0.5 mol%Cr_2O_3	1350 ℃, 1 h	87.42[a]	[39]
97.5 mol%ZnO+ 0.5 mol%Pr_6O_{11}	0.5 mol%Dy_2O_3	1.0 mol%CoO+0.5 mol%Cr_2O_3	1350 ℃, 1 h	66.6[a]	[40–45]
96 mol%ZnO+ 0.5 mol%Pr_6O_{11}	2.0 mol%Er_2O_3	1.0 mol%CoO+ 0.5 mol%Cr_2O_3	1340 ℃, 1 h	61.4[a]	[46]
97.5 mol%ZnO+ 0.5 mol%Pr_6O_{11}	0.5%La_2O_3	1.0 mol%CoO+ 0.5 mol%Cr_2O_3	1300 ℃, 1 h	81.6[a]	[47–50]

The nonlinear coefficient α_{max} was calculated from (*a*) $\alpha=[\log(V_{10mA}/V_{1mA})]^{-1}$ or (*b*) $\alpha=[\log(V_{1mA}/V_{0.1mA})]^{-1}$, while the calculation formula for (*c*) wasn't reported.

help to enhance the donor concentration, resulting in lower barrier height, and thus reducing the nonlinear coefficient of ZnO varistors [48,49].

The effect of doping amount of REs on the nonlinear coefficient of ZnO varistors is very complicated. Typical relationship curves between the doping amount of REs and nonlinear coefficient of ZnO varistors are schematically summarized in Fig. 2.

(1) When a ZnO–Bi_2O_3 varistor is doped with a certain amount of Pr [13–15], or a ZnO–Pr_6O_{11} varistor is doped with a certain amount of Dy [40,41,45], Er [55], Y [56,57], and so on, it will result in an effect as shown in Fig. 2(a). With such kind of REs doped, partial RE ions will enter into ZnO grains, resulting in substituting reaction of Zn^{2+} ions by RE ones there. During the substituting reaction, the produced oxygen will be easily absorbed onto ZnO grains, and the absorbed oxygen will marry with free electrons there, producing anions. The produced negatively charged oxygen (anion) is the major contributor to form the barriers in a varistor, which could heighten the barrier height of the varistor, thus enhancing the nonlinear coefficient. But because the substituting reaction in ZnO grains is limited, after too much of RE is doped into a ZnO varistor, most of the doped RE oxides will segregate the ZnO grain boundary, accumulating there excessively as inter-granular phase, finally leading to increased porosity of the samples, and decreasing their densification and structure homogeneity. Meanwhile, this process will expand the grain boundary width and reduce the barrier height, thus deteriorating the nonlinear characteristics of the varistor. However, the "pinning effect" of the doped REs can inhibit the growth of ZnO grains and thus improve the homogeneity of the sample, narrowing the distribution in the space of barrier height of grain boundary, decreasing their dispersity, eventually increasing the nonlinear coefficient.

(2) When a ZnO–Pr_6O_{11} varistor is doped with a certain amount of Nd [18] or La [47,48,50], or a ZnO–Bi_2O_3 varistor is doped with a certain amount of Ho [23], it will produce an effect as illustrated in Fig. 2(b). Like Y doping described in the above paragraph, after certain amount of the REs indicated here is doped, a substituting reaction will also happen, producing oxygen during the reaction, which is of benefit to the increase of nonlinear coefficient of the varistor. Meanwhile, after doping, the ZnO grains in the sample will become finer and more uniform, which is also of help to the improvement of nonlinear coefficient of the varistor. However, the substituting reaction will produce electrons as well, functioning in enhancing the donor concentration and reducing the barrier height, which will play a role in decreasing the nonlinear coefficient of the varistor. Moreover, after an excessive amount of REs is doped, the added RE

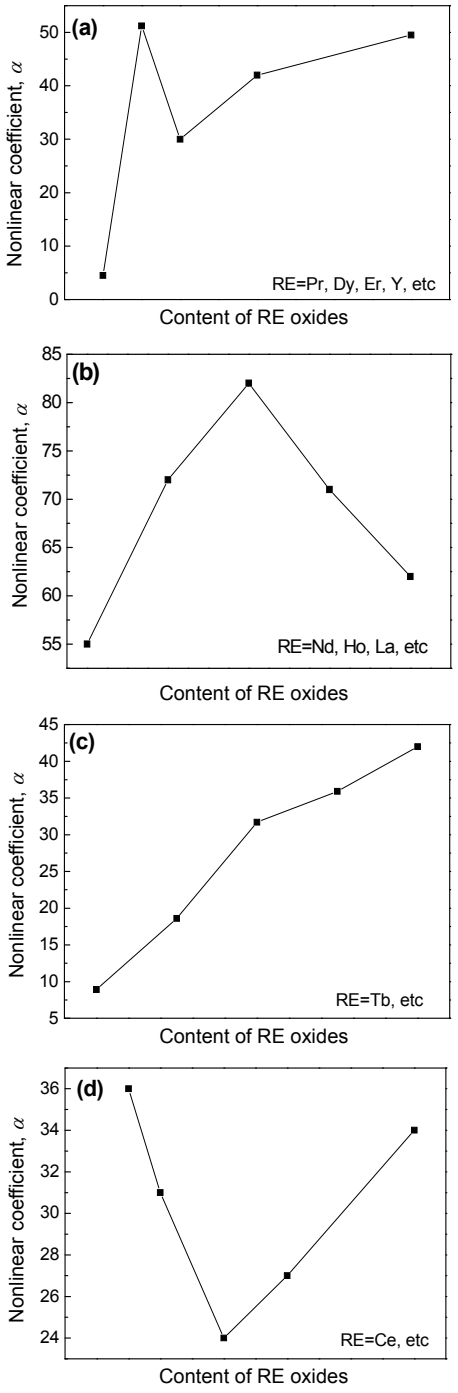

Fig. 2 Schematic relationship curves between nonlinear coefficient of ZnO varistors and doping amount of different RE oxides.

oxides will segregate the grain boundary of the sample, which will reduce the densification and structure homogeneity of the materials, leading to reduced barrier height and thus lower nonlinear coefficient of the varistor.

(3) Figure 2(c) presents the case of Tb doping in a ZnO–Pr_6O_{11} varistor [52,53]. Except the reasons mentioned above for the effect on a ZnO varistor after RE doping, the doped Tb_4O_7 will also decompose during sintering reaction, releasing O_2 during sintering, which is of much help to the increase of nonlinear coefficient of the varistor.

(4) Figure 2(d) illustrates the case of Ce doping in a ZnO–Bi_2O_3 varistor [30]. In such a series of varistors, the existence of a large number of pyrochlore phase will impose an adverse impact on the increase of nonlinear coefficient of the varistor. The reason for such phenomenon is that, pyrochlore phase is an unstable phase in the varistor under the flowing of a current, thus hot ion diffusion will occur, resulting in increased leakage current and reducing the nonlinear coefficient of the varistor. Simultaneously, when the pyrochlore phase is generated in cooling process, it will destroy the homogeneity of grain boundary structure of the varistor, thus deteriorating its nonlinear performance. After an appropriate amount of RE is doped, it will significantly reduce the productivity of pyrochlore phase, and promote the homogeneous distribution of Co^{3+}, Cr^{3+} and so on dissolved in the pyrochlore phase over the grain boundary of the sample, thus improving the nonlinear performance of the varistor.

4 RE doping effect on leakage current of ZnO varistors

Leakage current is the current flowing through a ZnO varistor during the normal working of circuit, where the nonlinear behavior of the varistor is not triggered. So, the lower the leakage current, the better the performance of a varistor. Table 3 lists some typical values of the leakage current of ZnO varistors after RE doping, which are reported in the literature in recent years.

Generally, leakage current varies inversely with nonlinear coefficient of the varistor, which is influenced by the current from hot ion diffusion. Such conducting process can be described by thermionic emission laws of Schottky barrier:

Table 3 Leakage currents of ZnO varistors doped with different REs

Practical composition			Sintering system	I_{min} (μA)	Ref.
Basic composition	RE added	Other additives			
81.84 wt%ZnO+ 2.79 wt%Bi_2O_3	7 wt%Pr_6O_{11}	5.58 wt%Sb_2O_3+0.465 wt%Cr_2O_3+ 1.395 wt%Co_2O_3+0.93 wt%MnO_2	1150–1200 ℃, 2 h	0.15[c]	[13–15]
96.5 mol%ZnO+ 0.5 mol%Pr_6O_{11}	2.0 mol%Nd_2O_3	1.0 mol%CoO	1300 ℃, 1 h	4.5[a]	[18]
96.5 mol%ZnO+ 0.7 mol%Bi_2O_3	0.5 mol%Er_2O_3	1.0 mol%Sb_2O_3+0.8 mol%Co_2O_3+ 0.5 mol%(MnO_2+Cr_2O_3+NiO)	800 ℃, 2 h	0.11[b]	[20]
97 mol%ZnO+ 0.5 mol%Pr_6O_{11}	1.0 mol%Tb_4O_7	1.0 mol%CoO+0.5 mol%Cr_2O_3	1300 ℃, 1 h	1.2[a]	[21]
95.65 mol%ZnO+ 1.0 mol%Bi_2O_3	0.8 mol%Ho_2O_3	0.5 mol%Co_2O_3+0.5 mol%$MnCO_3$+ 0.5 mol%Cr_2O_3+1.0 mol%Sb_2O_3+ 0.05 wt%$Al(NO_3)_3{\cdot}9H_2O$	1180 ℃, 2 h	0.8[a]	[23]
94.316 mol%ZnO+ 0.5 mol%Bi_2O_3	0.9 mol%CeO_2	1.2 mol%Sb_2O_3+0.5 mol%Co_2O_3+ 1.0 mol%MnO_2+0.5 mol%Cr_2O_3+ 0.5 mol%Ni_2O_3+0.5 mol%SiO_2+ 0.08 mol%B_2O_3+0.004 mol%Al_2O_3	1175 ℃, 2 h	~5[a]	[30]
90.0 mol%ZnO+ 0.5 mol%Pr_6O_{11}	4.0 mol%Y_2O_3	5.0 mol%CoO+0.5 mol%Cr_2O_3	1350 ℃, 1 h	0.047[a]	[39]
97.5 mol%ZnO+ 0.5 mol%Pr_6O_{11}	0.5%La_2O_3	1.0 mol%CoO+0.5 mol%Cr_2O_3	1300 ℃, 1 h	0.2[a]	[47–50]
96.5 mol%ZnO+ 0.5 mol%Pr_6O_{11}	0.5 mol%Dy_2O_3	2.0 mol%CoO+0.5 mol%Cr_2O_3	1350 ℃, 1 h	0.1[a]	[58–62]

The leakage current I_{min} was calculated from (*a*) 80% V_{1mA}, or (*b*) 75% V_{1mA}, while the calculation formula for (*c*) wasn't reported.

$$I = I_0 e^{-(E_i - \beta V^{1/2})/KT} \quad (1)$$

where I is the current flowing through the varistor; V is the electric field loaded on the varistor; T is the temperature; E_i is Schottky barrier height; I_0 and β are constants; and K is Boltzmann constant. It can be seen from Eq. (1) that, with increasing barrier height, the leakage current can be reduced [14]. Liu *et al*. [16] and Nahm *et al*. [56] also pointed out that, a high nonlinear coefficient is always accompanied with a low leakage current because of the high effect of tunneling current, and a low nonlinear coefficient is associated with a high leakage current due to the high thermionic emission current.

As mentioned in Section 3, although the ionic radius of REs is greater than that of Zn^{2+} ions, the substituting reaction of Zn^{2+} ions by RE ones will still happen in ZnO grains of the samples during sintering. In the substituting reaction, if oxygen is generated it will reduce the donor concentration, enhancing the barrier height, thus lowering the leakage current of the varistor; and if electrons are produced it would be of help to increase the donor concentration, lowering the barrier height, thus enlarging the leakage current. Moreover, too much of RE doping will also cause excessive accumulation of inter-granular phase in the ZnO grain boundary, producing more pores in the sample, reducing the densification and structure homogeneity of the sample, resulting in increased leakage current of the varistor.

Like the nonlinear coefficient of a ZnO varistor influenced by RE doping, the effect of doping amount of REs on the leakage current of the varistor is also very complicated. Typical relationship curves between the doping amount of REs and leakage current of ZnO varistors are schematically illustrated in Fig. 3, which are reported in recent years. Among them, Pr-doped ZnO–Bi_2O_3 varistors [13–15], or ZnO–Pr_6O_{11} varistors doped with Dy [40,41,45], Er [55] or Y [56,57] can present an effect as shown in Fig. 3(a); Fig. 3(b) shows the effect of ZnO–Pr_6O_{11} varistors doped with Nd [18] or La [47,48,50], or a ZnO–Bi_2O_3 varistor doped with Ho [23]; a ZnO–Pr_6O_{11} varistor doped with Tb can display an effect as illustrated in Fig. 3(c) [52,53]; and the effect of Ce doping into a ZnO–Bi_2O_3 varistor can be illustrated in Fig. 3(d) [30].

Taking the effect of RE doping on the nonlinear coefficient of ZnO varistors as illustrated in Section 3 into account, combined with the relationship between nonlinear coefficient and leakage current as shown in Eq. (1), one can easily understand the dependence of leakage current of a ZnO varistor on the doping amount of REs as illustrated in Fig. 3.

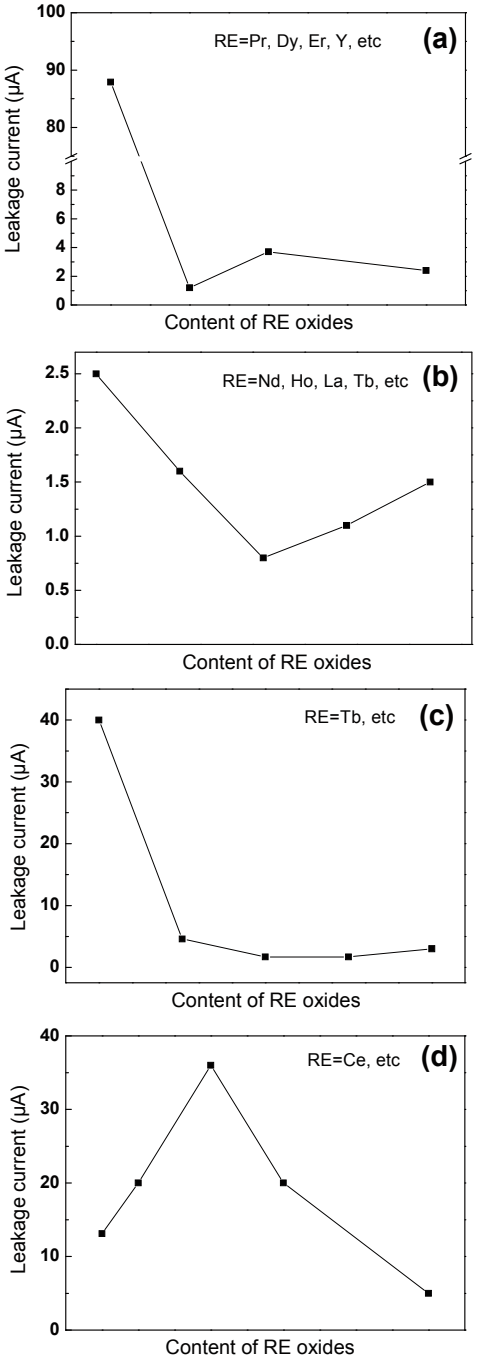

Fig. 3 Schematic relationship curves between the leakage current of ZnO varistors and doping amount of different RE oxides.

5 RE doping effects on through-current capability and energy absorption capacity of ZnO varistors

Due to the special working environment of surge

varistors (high current shock), there are two typical failure modes for a ZnO varistor: breakdown and bursting, in which breakdown is caused by fusion owing to the high local temperature where the current is concentrating, and bursting is induced by the mechanical stress stemming from the temperature gradient throughout the varistor. Under the impact of impulse current with different wavelengths and amplitudes, in order to obtain a wide protective margin, the through-current capability and energy absorption capacity to impact energy of ZnO varistors should be improved.

The through-current capability is the ability of a varistor to tolerate the current flowing through it (also called through-current capacity), which can, commonly, be described as an impulse current or wave current in certain amplitude.

The energy absorption capacity is usually calculated by the following formula:

$$E = CVIt \tag{2}$$

where E is the energy absorption capacity; V is the voltage loading on the varistor; I is the peak current flowing through the varistor (rush current); C is a constant depending on the wave shape of the current; and t is the duration of the current.

Literatures indicate that the main factor affecting the through-current capability of a varistor is the inhomogeneity of the varistor inner microstructure, which would lead to nonuniform distribution of the current, resulting in internal thermal stress due to the heat when the current flow through the varistor. Generally speaking, any local defects in a varistor should be reduced as less as possible, in particular, macropores in it. Therefore, in order to increase the flow capacity of the varistor, it is essential to improve the homogeneity of the varistor microstructure and thus enhance the uniformity of current distribution. From the viewpoint of material preparation, in order to ascertain a good nonlinear performance for a varistor, it is necessary to guarantee the consistence in chemical stoichiometry of the initial raw powders of high purity and the formed phase as required, a homogeneous microstructure distribution of the individual raw powders, and a reasonable range in particle size. To do so, it is, usually, to adopt an appropriate spray heat/granulation technology to gain more uniform composite powders with finer particles.

After RE doping, it can reduce the size of ZnO grains, produce more homogeneous microstructure distribution, and thus reduce the sample porosity of the varistor samples. Moreover, after RE doping, the formation path of spinel phase in the samples can be changed. Normally, the structure of spinel phase existing in a ZnO varistor sample without RE doping is in a cluster structure, but after RE doping, fine spinel phase grains will be formed, which can easily be distributed more homogeneously in the sample, thus increasing the energy absorption capacity of the varistor [8,11]. However, too much of RE doped will increase the difficulty to sinter the sample densely, enlarging the macro-pores and increasing the porosity of the sample, thus reducing the sample homogeneity, increasing the leakage current and decreasing the through-current capability of the varistor.

Reference [8] revealed that the energy absorption capacity of a varistor can be raised up to 7% by RE doping. Reference [11] indicated that the energy tolerance of a varistor can be heightened nearly two times with RE doping. Wang and Ma [63] studied the electrical properties of ZnO varistors doped with yttrium oxide, indicating that with increasing doping amount of yttrium oxide, the single energy absorption capacity of the varistor can be increased up to 246 J/cm^3 and the amplitude in wave current can be reached up to maximally 1000 A. Liu [64] reported that ZnO varistors doped with yttrium oxide are able to withstand long duration impulse current of 800 A, and the unit volume energy absorption capacity can be increased up to more than 40%.

6 RE doping effect on residual voltage of ZnO varistors

The so-called residual voltage is the voltage (surge voltage or impulse voltage) that appears across the resistor under the impact of impulse current. In general, the lower the residual voltage, the higher the protection level of the varistor. And there is another concept, residual voltage ratio, expressed as the quotient of residual voltage divided by voltage gradient (V_{1mA}), which can also characterize the nonlinear performance of the varistor. Usually, when the surge current is constant, the smaller the residual voltage ratio, the better the nonlinear performance of a varistor.

In the case of constant current waveform and amplitude, the residual voltage of a ZnO varistor is mainly determined by the impedance of its equivalent capacitance. Under the same current amplitude current, the residual voltage of the varistor basically depends

on its inductive impedance [65]. Li *et al*. [66] studied the relationship between the residual voltage ratio and varistor microstructure parameters, deduced a formula between the residual voltage ratio and average size of ZnO grains in the varistor sample, indicating that the smaller the ZnO grain size, the lower the residual voltage ratio of the varistor. After RE doping, the ZnO grain size in the sample would be decreased, resulting in increased number of microscopically paralleled equivalent capacitors, thus increasing the total equivalent capacitance. Because the impedance of the capacitor is inversely proportional to the capacitance, the impedance of the capacitor will be reduced, finally resulting in decreased residual voltage of the varistor. For example, it was confirmed in Ref. [8] that after RE doping, the inductive impedance of a varistor can be reduced.

Reference [12] introduced the development of ZnO arrester in Japan, pointing out that in RE-doped MOA chip varistors, the residual voltages of 154 kV series and 66 kV series MOA varistors are reduced up to 25% and 15%, respectively. So, it is of help to the miniaturization of MOA varistors. Huang *et al*. [28] reported the effect of yttrium doping on the electric properties of ZnO varistors, indicating that the residual voltage ratio of the varistors varies contrarily to the change trend in voltage gradient with Y doping, acquiring a minimum residual voltage ratio ($V_{1mA}/V_{0.1mA}$) of 1.12.

7 RE doping effect on *C–V* characteristic and dielectric property of ZnO varistors

Capacitance–voltage (*C–V*) relationship is an important interface characteristic of semiconductor materials, which can reveal the parameters of the materials and their devices, such as doping of a semiconductor, lifetime of carriers, interface state and so on. As for the *C–V* characteristic of ZnO varistors, the main researches are focusing on the relationships of barrier height or the width of depletion layer with donor concentration and interface state density [67,68].

The barrier height is related to the donor concentration N_d and interface state density N_t. Typically, the value of barrier height will be enhanced with increasing N_t or reducing N_d, and the width of depletion layer changes contrarily to the varying tendency of N_d.

C–V characteristic is generally measured at 1 kHz; and the donor concentration N_d and barrier height Φ_b are determined by the following formula [67]:

$$\left(\frac{1}{C_b}-\frac{1}{C_{b0}}\right)^2=\frac{2}{q\varepsilon N_d}(\Phi_b+V_g) \tag{3}$$

where C_b is the capacitance of grain boundary per unit area; C_{b0} is the capacitance when $V_g=0$; V_g is the voltage of single grain boundary; q is the electronic charge; and ε is the dielectric constant of ZnO ($\varepsilon=8.5\varepsilon_0$, in which ε_0 is the vacuum dielectric constant).

The interface state density N_t of a varistor can be calculated by the following formula [67]:

$$N_t=\sqrt{\frac{2\varepsilon N_d\Phi_b}{q}} \tag{4}$$

And the width of depletion layer, t, is determined by the following formula [67]:

$$N_d t=N_t \tag{5}$$

As described in Section 3, although the ionic radius of RE atoms is greater than that of Zn^{2+} ions, the substituting reaction of Zn^{2+} ions by RE ones will still happen in ZnO grains, generating lattice defects there. Moreover, during the substituting reaction, oxygen will be produced, which will reduce the donor concentration of the varistors. As seen in Eq. (3), the barrier height will be enhanced, and the interface state density will be reduced as calculated from Eq. (4). However, the donor concentration N_d changes more dramatically than the interface state density N_t does. Therefore, as calculated from Eq. (5), the depletion layer width will be increased. And if electrons are produced during the substituting reaction after RE doping, it would be of help to enhance the donor concentration of the varistors, driving the interface state density increased, thus reducing the barrier height and width of the depletion layer of the varistors.

The dielectric properties of ZnO varistors reveal not only the law of capacitance and dielectric loss tangent with temperature, frequency and other factors, but also the microstructures of the varistors.

Literatures indicate that the relative dielectric constant ε of a varistor can be correlated directly with the ZnO grain size of the sample, as expressed by

$$\varepsilon=\varepsilon_g\left(\frac{d}{t}\right) \tag{6}$$

where ε_g is the dielectric constant of ZnO; d is the ZnO grain size; and t is the width of depletion layer. Thus, the larger the ZnO grain size, the greater the relative

dielectric constant. In general, the dielectric loss tangent consists of the heat loss caused by leakage current and friction heat loss induced by electric dipole rotation. When the heat loss caused by leakage current becomes obvious, the dielectric loss tangent is relatively large.

Generally, RE doping will inhibit the growth of ZnO grains. As shown in Eq. (6), the relative dielectric constant of a ZnO varistor varies with the ZnO grain size, in a rule consistent with the dependency of voltage gradient on RE doping amount. The dielectric loss tangent is determined mainly by leakage current, in a rule consistent with the relationship of the leakage current of the varistor with the RE doping amount.

8 Conclusions and outlook

RE doping can significantly improve the electrical properties of ZnO-based varistors, such as voltage gradient, nonlinear coefficient, leakage current, through-current capability and so on, when an optimum amount of REs is doped. These properties depend on the microstructure and homogeneity of the varistors. High voltage gradient and through-current capability can improve the performance of ZnO varistors in the field of high voltage application, which are also conducive to the miniaturization of metal oxide arresters, already showing broad application prospects.

The future focus of RE doping into ZnO varistors can be summarized as following:

(1) New optimized prescription of ZnO varistor materials with RE doping is still welcome. The purpose of such work is to develop new materials with high voltage gradient and large energy absorption capacity, so as to manufacture varistors suitable for applications in ultrahigh voltage power transmission with minimal devices.

(2) New emphasis should be paid on improvement mechanism of RE doping into ZnO varistors, for the sake of avoiding abuse or misuse of REs.

(3) Further theoretical and experimental studies should be carried out to clarify the "soft heart" phenomenon in large-size ZnO–Bi_2O_3 varistors with RE doping.

(4) Through applying modern high-energy ball milling technology, nanotechnology, microwave sintering technology and other advanced fabrication technologies, it can effectively reduce the sintering temperature of ZnO varistors, enhancing the microstructure homogeneity of the sintered varistor samples, thus further improving the material properties and promoting the industrialization of the new materials.

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